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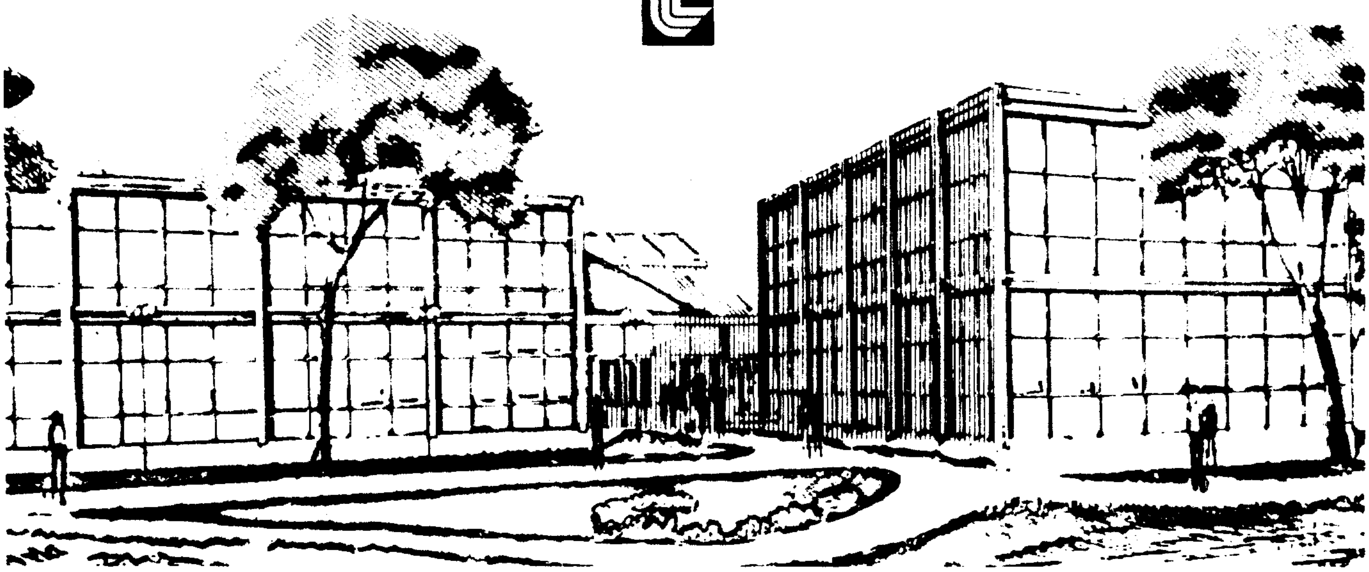

SPACE-CHARGE-LIMITED CURRENT AND CAPACITANCE IN Cu_xS/CdS SOLAR CELLS*

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ABSTRACT

The unusual behavior of Cu_xS/CdS solar cells is better described with space-charge-limited current (SCL I) than with standard junction models. The SCL I theory provides the first quantitative explanation of these devices' I-V characteristics including their non-exponential form, the dark-light crossover, the temperature independent slope in addition to qualitatively modeling the voltage variation of capacitance. This is accomplished with trapping parameter values well known to be characteristic of Cu compensated CdS. It indicates that the voltage dependence of current is controlled by mechanisms entirely different than previously proposed with important implications for device fabrication and optimization and ultimate device performance.

INTRODUCTION

The unusual electrical properties of Cu_xS/CdS solar cells have long presented characteristics that have been difficult to model quantitatively. Gross behavior such as the dark-light crossover of the I-V, the non-exponential dependence of I on V, and the temperature independent slope of the I-V (1-5) have not been adequately explained. Analysis of this paper shows that such behavior is well described by a space-charge-limited current (SCL I) model that is controlled by physical mechanisms that are distinctly different from those involved in standard models (4-7).

THEORY

SCL I models have distinctive voltage and temperature dependences unlike that of standard theories. Qualitatively SCL I has a voltage dependence that sequentially shows I proportional to V, V^m ($m>2$), and finally V^2 for increasing current (8). This I-V shape is preserved at any temperature as long as SCL I mechanisms dominate. The capacitance for the linear, resistive region is just its geometric value $\epsilon A/L$ independent of voltage. Here ϵ is the dielectric constant, A is the cross-sectional area and L is the width SCL I region. For the $I \propto V^2$ region, SCL I theory shows that this capacitance is increased by the factor 3/2 (8). The transition between these values occurs in the $I \propto V^m$ interval. Empirically this transistion has been observed to involve a sharp drop in capacitance for SCL I produced in thin film, polycrystalline CdS (9).

The quantitative relations between current and voltage with an arbitrary distribution of traps is obtained with numerical integration. Considering the simplest case of a highly compensated CdS layer (due to Cu acceptors) of width L with uniform concentrations of equilibrium conduction electrons n_o and electron traps N_{ti} with the traps located on an energy E_c-E_{ti} below the conduction band edge, allows Gauss's law for the region to be written as

$$\frac{d\xi(x)}{dx} = -\frac{e}{\epsilon}\left[n(x) - n_o - \sum_i \left\{p_{ti}(x) - p_{tio}\right\}\right] \tag{1}$$

where $\xi(x)$ is the electric field, x is the space variable, e is the electronic charge, n(x) is the non-equilibrium conduction electron concentration, and $p_{ti}(x)$ and p_{tio} are the non-equilibrium and equilibrium concentrations of holes in the ith trap respectively. It is implicitly assumed in this expression that the build-up of non-equilibrium space charge is so dominant that the presence or absence of a small initial, equilibrium space charge has negligible effect on the results. This is reasonable for the small equilibrium space charge present in a highly compensated and depleted CdS layer.

The second assumption, that is standard for SCL I (8), is that current is dominated by drift alone so the current density can be used to specify the carrier concentration by

$$n(x) = \frac{J}{e\mu\xi(x)} \tag{2}$$

where J is the current density and μ is the mobility. Substituting this back into Eq. 1 gives the primary differential equation as

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$$\frac{d\xi(x)}{dx} = -\frac{J}{e\mu\xi(x)} + \frac{n_o e}{\epsilon} - \frac{e}{\epsilon}\sum_i N_{ti} \cdot$$

$$\left[\frac{1}{\frac{2n_o}{N_i}+1} - \frac{1}{\frac{2J}{N_i e\mu\xi(x)}+1}\right] \tag{3}$$

since

$$p_{ti}(x) = N_{ti}\left(1 - \frac{1}{1+\frac{1}{2}e^{\frac{E_{ti}-E_{fn}(x)}{kT}}}\right)$$

$$= \frac{N_{ti}}{\frac{2n(x)}{N_i}+1}$$

$$= \frac{N_{ti}}{\frac{2}{N_i}\frac{J}{e\mu\xi(x)}+1} \tag{4}$$

with N_i defined by

$$N_i = N_c\, e^{-\frac{E_c - E_{ti}}{KT}} \tag{5}$$

so that

$$\frac{n(x)}{N_i} = e^{-\frac{E_{ti}-E_{fn(x)}}{KT}} \quad . \tag{6}$$

Here $E_{fn}(x)$ is the quasi-Fermi level for conduction electrons and N_c is the effective density of states (10). Similarly

$$p_{tio} = \frac{N_{ti}}{\frac{2n_o}{N_i}+1} \quad . \tag{7}$$

The required single boundary condition for finding $\xi(x)$ is (see Eq. 2)

$$\xi(o) = \frac{J}{e\mu n(o)} \tag{8}$$

The third assumption, also standard for SCL I (8), is that $n(0) >> 1$. This condition was found to be sufficiently satisfied for accurate numerical integration of Eq. 3 to give $\xi(x)$ when $n(o) = 10^5\, n_o$. Again numerically integrating this $\xi(x)$ result finally gives the voltage V for a specified J as

$$V = -\int_0^L \xi(x)dx. \tag{9}$$

Note that this current-voltage relationship is totally specified by the concentrations n_o and N_{ti}, the energy spacings $E_c - E_{ti}$, the compensation width L, and the mobility μ.

In contrast, standard treatments of P-N junction transport indicate that current is exponentially related to voltage divided by temperature T (6,7). Tunneling models indicate that current is rather independent of T and the simplest treatments show that it is exponentially related to voltage (4,5). However quite varied relationships between I-V are seen in tunneling devices such as Zener and tunnel diodes so that a single required tunneling characteristic can not be specified.

RESULTS

Cu_xS/CdS samples A and B were fabricated at Lawrence Livermore onto a vacuum deposited CdS substrate with the Cu_xS layer formed by reactive sputtering. Sample C was constructed by the University of Delaware's Institute of Energy Conversion by wet-dip formation of the Cu_xS layer onto a vacuum deposited CdS layer. All samples were extensively heat treated.

Figure 1 shows the dark and light (simulated AM1) J-V characteristics measured on sample A. For convenience, the short circuit current density J_L has been added to the light data to make $J + J_L$ go to zero when V is zero. This allows plotting all the data on the same logarithmic scales. Note that both data sets exhibit the distinctive V and V^m regions with the light data also showing the V^2 region of SCL I for current variations over 4 to 6 orders of magnitude. Measuring J in the light near zero voltage involved currents in the mA/cm^2 so that current changes less than 10^{-2} mA/cm^2 were not measureable for the light data.

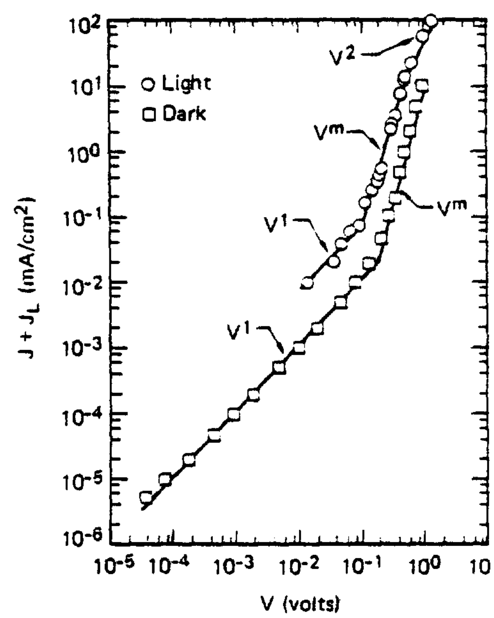

Fig. 1. The dark and light (AM1), current-voltage characteristics of sample A that demonstrate the distinctive SCL I behavior.

Similar measurements as a function of T were taken on sample B and plotted in Fig. 2. In addition to the V and V^m regions, the temperature independent slopes characteristic of SCL I are clearly shown. The curves definitely do not exhibit exponential dependence on V/T. All of the published data of temperature dependent J-V curves for Cu_xS/CdS cells have shown similar results with none demonstrating the exponential 1/T behavior (3-5, 11).

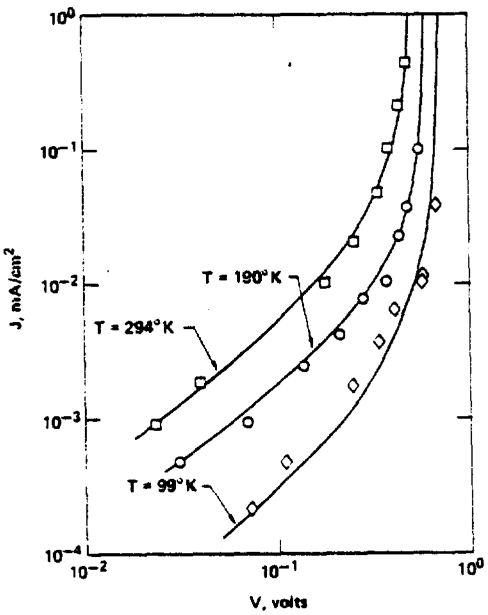

Fig. 2. The temperature dependent, current-voltage properties of sample B that show the T independent slope characteristic of SCL I.

The dark and light J-V properties measured on sample C are shown as the data points in Fig. 3 demonstrating the same properties as sample A. The theoretical fit of this data by the numerical integration, SCL I model is shown by the solid curves. For the theoretical curve, it was assumed that the short circuit current superimposes on the SCL I with light exposure. The parameters that gave this fit are $n_0 = 2.7 (10^{10})cm^{-3}$ (light) and $9(10^9)cm^{-3}$ (dark), $\mu = 20\ cm^2/V$ sec (light) and $7\ cm^2/V$ sec (dark), $N_{t1} = 1.3(10^{14})\ cm^{-3}$ (light) and $7(10^{14})\ cm^{-3}$ (dark), $E_c - E_{t1} = 0.30$ eV, $N_{t2} = 5.1\ (10^{14})\ cm^{-3}$, $E_c - E_{t2} = 0.44$ eV, $L = 1.33(10^{-4})$ cm, $\epsilon/\epsilon_0 = 10$, $m_n^*/m_o = 0.2$, and T = 294°K. The L was determined from zero bias, dark capacitance. The m^* and m_o are the conduction electron's effective and free masses respectively. These parameter values are typical of those reported for CdS. The trap levels and densities are close to those measured by Grill et al(12) on single crystal CdS using DLTS. The dark n_o and μ values and their change in light are approximately those found by Wu and Bube (13) on Cu compensated, polycrystalline CdS using thermoelectric techniques. Similar SCL I behavior was found in p-GaAs/n-ZnSe heterojunction solar cells as reported by Balch and Anderson(14).

When this sample C data and theory are plotted on linear scales the excellent agreement shown in Fig.4 is obtained. This graph shows that sample C_2 has an efficiency of 6.1 percent, a J_L of 17 mA/cm², an open circuit voltage of 0.51 V, and a fill factor of 0.70. To the best of our knowledge this model provides the first quantitative fit of this dark-light crossover behavior that is characteristic of Cu_xS/Cds solar cells. This same crossover is seen when the Fig. 1 data is replotted on linear scales. The dark capacitance-voltage properties of sample C were obtained far into forward bias region using a transient technique similar to that of Dresner and Shallcross (9) with an accuracy that is undiminished by large current flow. The results are shown in Fig. 5 for various heat treatment times given the cell at 180°C in air. Note the sharp drop in capacitance at around 0.3 to 0.4 volts. From Fig. 3 this corresponds to the V^m region where an anomaly is theoretically indicated and where such behavior has been previously observed with SCL I(9).

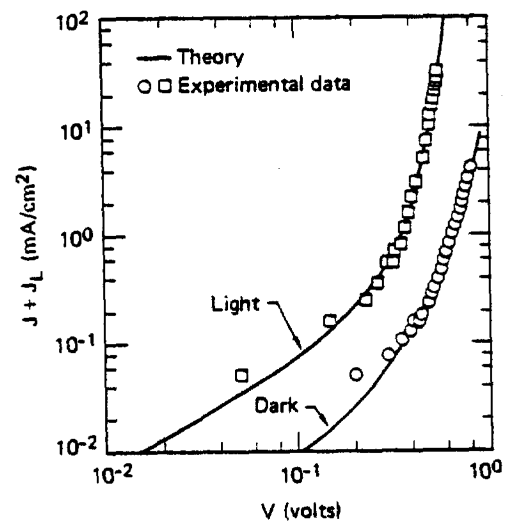

Fig. 3. Logarithmic plot of the current-voltage properties of sample C as shown by the data points for the dark and light. The solid curves are the SCL I theory fit obtained with numerical integration.

CONCLUSIONS

Measurements taken on Cu_xS/CdS solar cells of up to 6 percent efficiency fabricated by two different processes at different locations indicate that the I-V characteristics as a function of temperature and light and the C-V behavior demonstrate the highly distinctive properties of SCL I. The current data definitely do not have the exponential V/T dependence of standard P-N junction models (6,7) or the exponential V variation of simple tunneling models (4,5). While tunneling current can exhibit a wide variety of behavior, it would be highly fortuitous if it had exactly the same properties as SCL I. Such I-V mimicing by tunneling has never been reported to the best of our knowledge. The fit that the SCL I model gives for the data is the first quantitative agreement that has been obtained for the dark and light properties. This was accomplished with parameter values well known to be characteristic of the involved materials and is in a form like that seen for another heterojunction solar cell.

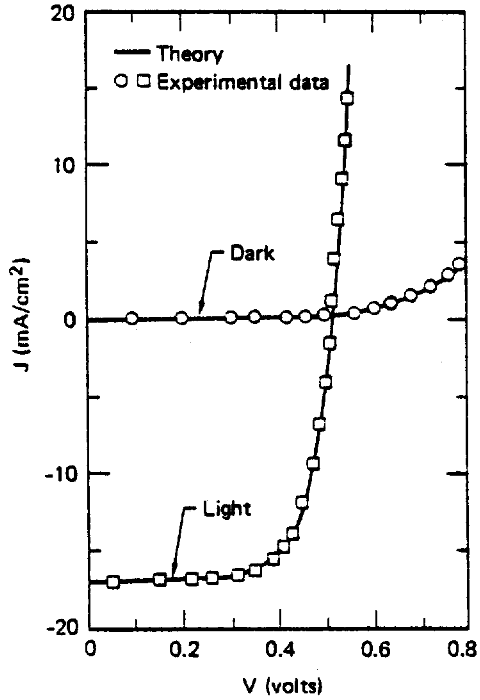

Fig. 4. Linear plot of sample C's measured data points and the numerical integration, SCL I theory given by the solid curves.

This indicates that the trap structure in the Cu compensated CdS layer controls the voltage dependence of current rather than the mechanisms of standard junction theory. Since these parameters have never been monitored in cells, they likely account for the non-repeatability often encountered. New calculations of ultimate device performance based on these results appear to be in order. This SCL I analysis is new so that only part of the cell behavior has been modeled so far. Continuing work is proceeding to use this approach to treat minority carrier collection, the energy band diagram, the reverse bias characteristics, and the photocapacitance.

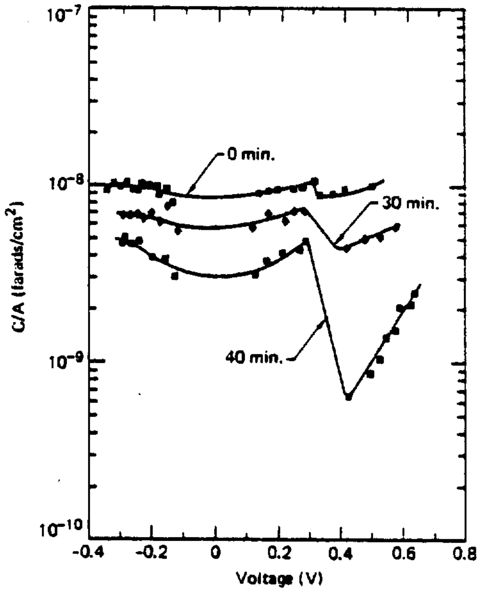

Fig. 5. The dc bias voltage dependence of sample C's small signal capacitance measured with a transient technique.

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